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Spectroscopy of a single adsorbed atom

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We have used a low-temperature ultrahigh-vacuum scanning tunneling microscope to perform atomically localized spectroscopic measurements on single Fe atoms adsorbed onto the Pt(111) surface. Using a simple tunneling model, we are able to quantitatively deconvolute the tip and adatom local densities of states (LDOS) from the dI/dV spectra. We find that a resonance occurs in the adatom LDOS that is centered 0.5 eV above the Fermi energy. This feature has a width of approximately 0.6 eV, and occurs only when the tip is within angstroms (laterally) of the center of an Fe adatom.

The discrete, localized states of an isolated atom are known to spread into broad resonances as the atom contacts a metal surface.[1,2] The energy, width, and orbital geometry of such resonances play an important role in determining many of an adatom's most important properties. These include the binding energy, work function, dipole moments, and equilibrium separation distance of the adatom.[1–4] Until recently, the only methods for spectroscopically probing the electronic structure of an adatom involved either averaging over a macroscopic area,[5] or the use of field emission.[6] Now, however, with the scanning tunneling microscope (STM), it is possible to perform local spectroscopic measurements with atomic-scale resolution.[7] This technique has been used to probe the electronic structure of various adsorbates on semiconductor surfaces,[8–11] but surprisingly little work has been done on metals.[12] One reason for this is the necessity to cool the surface due to adatom mobility at higher temperatures. Coupled with the STM's ability to manipulate single adatoms on metal surfaces,[13,14] atom-localized spectroscopy on metals is likely to provide a powerful tool for the characterization of man-made nanometer-scale structures in the future.

We report here a spectroscopic study of *single metal adatoms* on a clean metal surface using an STM. Atomically localized spectroscopic measurements were performed on single, well-separated Fe adatoms on the Pt(111) surface. We find that a narrow resonance occurs in the adatom local density of states (LDOS) that is centered 0.5 eV above the Fermi energy (E_F). Both the spatial extent of this resonance as well as its effect on the apparent height of the adatom were measured. Differential conductivity (dI/dV) spectra were recorded using different STM tips, and were found to be strongly tip dependent. However, by using a deconvolution scheme that is based upon a simple tunneling model,[15] we are able to quantitatively deconvolute the surface and tip state densities. We find that although the electronic structure of different tips varies greatly, the deconvolution procedure yields a largely tip-independent LDOS at the site of an Fe adatom.

The experiments were performed using an STM contained in ultrahigh vacuum and cooled to 4 K.[13,14] The single-crystal Pt sample was prepared by Ar-ion sputtering followed by annealing to 900 °C for several minutes. The Auger-clean sample was then cooled to 4 K and dosed using a calibrated electron-beam Fe evaporator. The convention used here is that the bias across the tunnel junction (V) is the voltage of the sample measured with respect to the tip. dI/dV spectra were measured through lock-in detection of the ac tunnel current driven by a 205-Hz, 3–10-mV (rms) signal added to the junction bias. While the tip of the STM is macroscopically a polycrystalline tungsten wire, the chemical identity of the outermost tip atoms was unknown for all measurements.

Figure 1 shows a 250×250 Å^2 image of the Pt(111) surface after dosing with 0.005 monolayer of Fe. Terraces on the surface were typically 40–400 Å wide, and separated by monatomic steps. The Fe adatoms can be seen as bumps having almost half the height of the Pt steps.[16] For low tunnel currents ($I \leq 1$ nA) and low bias voltages ($V \approx 0.1$ V), the adatoms do not move from scan to scan. Low junction impedance ($V/I \leq 70$ kΩ) or high bias voltage ($V \geq 0.5$ V), however, often resulted in tip-induced motion of the Fe adatoms along the terrace.

Figure 2 shows normalized dI/dV spectra of the tunnel junction measured both with the tip over the centers of Fe adatoms ("on Fe"), and with the tip over nearby bare Pt spots ("off Fe"). Data were collected for three

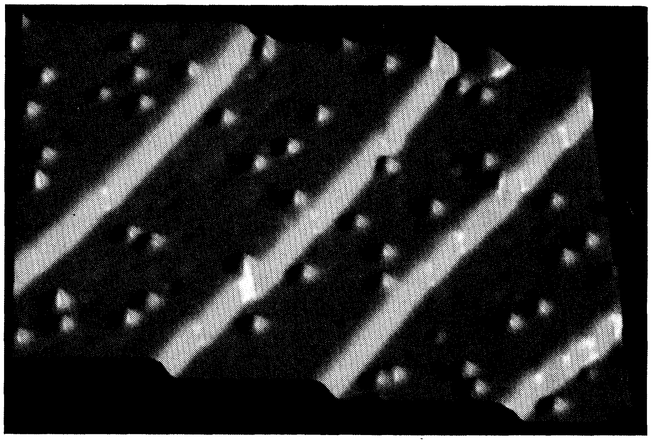

FIG. 1. Constant current 250×250 Å^2 image of the Pt(111) surface after adsorption of ~0.5% monolayer of Fe at 4 K. Image was taken with tunnel current of 0.13 nA and junction bias of 0.1 V. About 46 Fe adatoms are visible as 0.9-Å bumps.

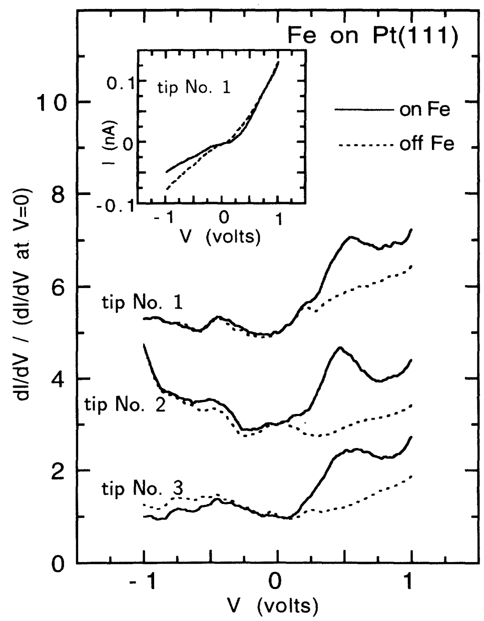

FIG. 2. Average dI/dV spectra (normalized at $V=0$) taken with STM tip over Fe adatoms (on Fe) and over nearby bare Pt surface (off Fe). Data taken with three different tips are shifted vertically. Inset: I-V characteristics taken with tip No. 1 on and off of a single Fe adatom.

different tips, each tip producing an average "on Fe" spectrum and an average "off Fe" spectrum. Tips are referred to as "different" if the microscopic configurations of the outermost atoms are different. Different tips were prepared *in situ* from the same macroscopic tungsten wire by various techniques, including field emission, gentle collisions with the surface, and tunneling at high currents ($I \geq 1$ μA).

The "on Fe" data were taken by first centering the tip over an Fe atom with tunneling parameters $I=0.13$ nA and $V=1.0$ V. A spectrum was then recorded by ramping the junction bias from 1.0 to -1.0 V with the STM tip held stationary (i.e., with the feedback loop opened).[17] The "off Fe" data were taken next by shifting the tip laterally by approximately 15 Å to a bare Pt spot and repeating the measurement process. This procedure was performed on 9–11 different Fe atoms for each of the three tips (measured adatoms were at least 10 Å away from step edges). Occasionally during measurement of a spectrum the adatom would jump laterally by approximately one lattice spacing. Spectra including such "jump events" were not included in the average.

There are three important points to note regarding the spectra in Fig. 2: (a) There is a peak in the on Fe spectra that disappears when the tip is moved off of the Fe adatom. The peak is centered at $V=0.5$ V and has a full width of about 0.6 V for all three tips. (b) The on Fe and off Fe spectra match closely for V far from the 0.5-V peak. This is true for each tip. (c) Aside from the peak at 0.5 V, much unrelated structure can be seen upon comparison of the spectra from one tip to another. Such tip-dependent behavior has been noted in other STM studies,[18,19] but here we again emphasize that changes in the structure of the apex of the tip can lead to drastic changes in the measured dI/dV spectra. The dI/dV spectra shown in Fig. 2 by no means span the entire range of tip-dependent behavior we have observed.

The inset to Fig. 2 shows current-voltage characteristics (I-V's) taken both on and off of a single Fe atom with tip No. 1. Each I-V is the result of measuring the dc tunnel current during a single voltage ramp in the manner described previously for the dI/dV spectra.

Figure 3(a) shows the spatial variation in tip height obtained from a constant current line scan across the top of an Fe adatom located near a step edge. The Fe adatom appears as a 1.2-Å bump with a width of 7 Å (full width at half maximum). The apparent height of the Fe adatom is measured as the distance between the top of the ad- atom peak and the average surrounding substrate level. For a given tunnel current and bias, differences in tip structure and surface site caused the apparent height of the adatoms to vary by ±10%.

The bias dependence of the apparent height of a single Fe adatom at $I=1.0$ and 0.1 nA can be seen in the inset to Fig. 3(a). Tip No. 1 was used for this measurement, but the adatom is different from that shown in Fig. 3(a). The adatom height has a slight shoulder at ~ -0.3 V and a sharp increase at 0.5 V, where the peak occurs in the dI/dV spectra.

The spatial extent of features in the dI/dV spectra can be measured by recording dI/dV while scanning the tip in the constant current mode. Figure 3(b) shows the spatial variation in dI/dV obtained simultaneously with the tip height variation shown in Fig. 3(a). This was measured by monitoring the ac tunnel current during the line scan (the ac frequency was kept too high for the feedback loop to respond). Since the junction was biased at

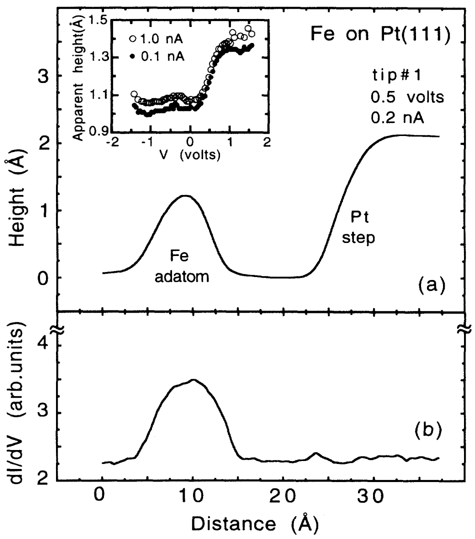

FIG. 3. (a) Height of STM tip during line scan across top of Fe adatom and Pt step edge using tip No. 1 ($V=0.5$ V and $I=0.2$ nA). (b) Spatial dependence of junction dI/dV, measured simultaneously with line scan shown in (a). Inset: Apparent height of a single Fe adatom vs V, measured at $I=1.0$ and 0.1 nA with tip No. 1.

$V=0.5$ V during the scan, Fig. 3(b) gives a spatial map of the peak seen in the dI/dV spectra at this bias. Through comparison to Fig. 3(a), it can be seen that the spatial variation of dI/dV closely follows the trajectory of the tip in the vicinity of the Fe adatom. The peak in dI/dV at $V=0.5$ V thus appears to be quite well localized to the adatom.

It is interesting to note that dI/dV at $V=0.5$ V remains roughly constant as the tip traverses the Pt step edge. While dI/dV is strongly sensitive to the presence of a single Fe adatom, it is negligibly affected by Pt surface features as large and abrupt as step edges. By "tuning" to an Fe adatom, one is thus able to use the differential conductivity as a tool to separate the Fe adatoms from other surface features. dI/dV measurements were used, for example, to spectroscopically distinguish atoms dropped intentionally from the tip (possibly W adatoms) from nearby Fe adatoms.[20]

The data can be analyzed using a simple tunneling model discussed by Lang in Ref. 15. Lang finds that the following expression provides a useful approximation to the tunnel current between the last atom on an STM tip and an adatom on a metal surface:

$$I(V) \propto \int_{E_F}^{E_F+|e|V} dE\, \rho_t(E-|e|V)\rho_S(E) \times e^{(-2s\sqrt{m}/\hbar)\sqrt{2(\phi+E_F-E)+|e|V}} \quad . \quad (1)$$

Here s is the distance between surface and tip electrodes, ϕ is the work function, m and $|e|$ are the mass and charge of an electron, $\rho_t(E)$ is the local density of tip states, and $\rho_S(E)$ is the local density of states at the surface. ϕ and E_F are taken as independent of electrode. For our purposes, $\rho_S(E)$ can represent the LDOS at either a bare spot on the Pt surface $[\rho_{\mathrm{Pt}}(E)]$ or the site of an Fe adatom $[\rho_{\mathrm{Fe}}(E)]$.

A key feature of our deconvolution scheme is the use of the bare surface as a reference electrode, that is, $\rho_{\mathrm{Pt}}(E)$ must be known. Here we will take $\rho_{\mathrm{Pt}}(E)$ to be constant.[21] Equation (1) can then be used to extract experimental values of $\rho_t(E)$ and $\rho_{\mathrm{Fe}}(E)$ from the dI/dV spectra (to within a multiplicative factor). The first step in this deconvolution is performed by taking a spectrum measured over the bare Pt surface (off Fe), and then using it to solve Eq. (1) numerically for $\rho_t(E)$. One can then use the extracted $\rho_t(E)$ in conjunction with an on Fe spectrum to similarly obtain $\rho_{\mathrm{Fe}}(E)$. The dI/dV spectra thus yield $\rho_t(E)$ and $\rho_{\mathrm{Fe}}(E)$ for any given tip. $\rho_{\mathrm{Fe}}(E)$ should, of course, be tip independent.

This deconvolution process was carried out for the spectra taken with tips Nos. 1–3. A 4.5-eV work function was used, along with a 6-Å electrode separation (corresponding to the experimental junction impedance of $\sim 10^{10}$ Ω). The results, however, are not sensitive to the work function or electrode separation. Figure 4 shows the tip and surface state densities extracted numerically from the dI/dV spectra. Figure 4(a) shows the extracted $\rho_t(E)$ for tips Nos. 1–3 (normalized at $\varepsilon=E-E_F=0.5$ eV). The electronic structure varies dramatically from tip to tip (the constant-current spatial images obtained from these three tips, though, were all quite similar).

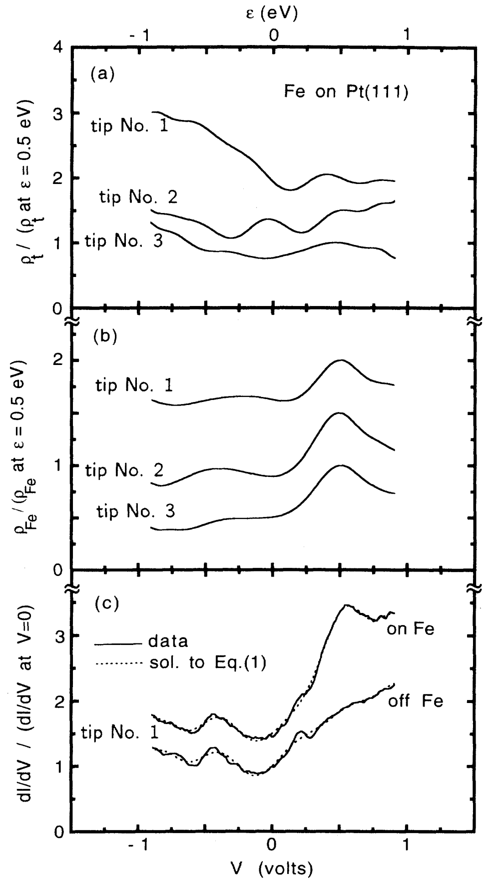

FIG. 4. (a) Normalized tip LDOS and (b) normalized surface LDOS at site of Fe adatom, extracted from dI/dV spectra for tips Nos. 1–3 (curves shifted vertically). (c) Solid lines: normalized dI/dV spectra measured on and off of Fe adatoms with tip No. 1 (curves shifted vertically). Dashed lines: calculated normalized dI/dV spectra for tip No. 1 on and off of an Fe adatom (see text).

Figure 4(b) shows the extracted $\rho_{\mathrm{Fe}}(E)$ for tips Nos. 1–3. Here, in contrast to $\rho_t(E)$, the curves obtained from the different tips are very similar. For $\varepsilon<0$ (filled states), $\rho_{\mathrm{Fe}}(E)$ is nearly constant, although there is a shallow rise centered at approximately $\varepsilon \approx -0.35$ eV. The most striking feature occurs for $\varepsilon>0$ (empty states) where the peak seen in the dI/dV spectra is reflected strongly here in the surface LDOS.

Figure 4(c) is provided to show the quality of the solution to Eq. (1) given by the state densities shown in Figs. 4(a) and 4(b). The solid lines show the normalized dI/dV measured both on Fe and off Fe with tip No. 1, as in Fig. 2. The broken lines show the calculated normalized dI/dV traces obtained when the extracted $\rho_t(E)$ and $\rho_{\mathrm{Fe}}(E)$ for tip No. 1 are substituted back into Eq. (1) [and Eq. (1) is differentiated with respect to V]. The solutions for tips Nos. 2 and 3 give similar agreement (not shown here).

The spatial dependence of dI/dV at $V=0.5$ V [Fig. 3(b)] is consistent with an unoccupied resonant state providing added state density local to the Fe adatom. The steplike increase in adatom height occurring at $V=0.5$ V (Fig. 3 inset) similarly corresponds to the predicted behavior of an adatom's apparent height when the bias is swept through a narrow resonance.[22]

There is reason to believe that the resonance centered at $\varepsilon \approx 0.5$ eV originates from an Fe s orbital. Lang has calculated the added state density due to the adsorption of a "prototype" transition-metal atom (Mo) onto a jellium surface.[22] He finds that the transition-metal adatom induces a narrow d resonance (~ 1 eV wide) slightly below E_F, and a broader s resonance (~ 2 eV wide) centered approximately 1 V above E_F. The calculated tunnel current is sensitive only to the s resonance, suggesting that the peak seen in the experimental Fe LDOS originates from the s resonance. In addition, other theoretical[3] and experimental[23] work (taking spin polarization effects into account) place the spin-split d resonance of Fe impurities in Ag mostly below E_F.

We note that the ability to measure atomic resonances *atom by atom* may yield a useful means of identifying chemically different adsorbates even when they might appear similar in STM topographs.

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[1] J. W. Gadzuk, Phys. Rev. B **1**, 2110 (1970).

[2] N. D. Lang and A. R. Williams, Phys. Rev. B **18**, 616 (1978).

[3] R. Podloucky, R. Zeller, and P. H. Dederichs, Phys. Rev. B **22**, 5777 (1980).

[4] N. D. Lang, Phys. Rev. Lett. **46**, 842 (1981).

[5] A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, 1988).

[6] E. W. Plummer and R. D. Young, Phys. Rev. B **1**, 2088 (1970).

[7] R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. Lett. **56**, 1972 (1986).

[8] R. M. Feenstra, Phys. Rev. Lett. **63**, 1412 (1989).

[9] P. N. First, J. A. Stroscio, R. A. Dragoset, D. T. Pierce, and R. J. Celotta, Phys. Rev. Lett. **63**, 1416 (1989).

[10] I.-W. Lyo and P. Avouris, Science **245**, 1369 (1989).

[11] P. Bedrossian, D. M. Chen, K. Mortensen, and J. A. Golovchenko, Nature **342**, 258 (1989).

[12] *Scanning Tunneling Microscopy and Related Methods,* edited by R. J. Behm, N. Garcia, and H. Rohrer (Kluwer, Dordrecht, 1990).

[13] D. M. Eigler and E. K. Schweizer, Nature **344**, 524 (1990).

[14] D. M. Eigler, C. P. Lutz, and W. E. Rudge, Nature **352**, 600 (1991).

[15] N. D. Lang, Phys. Rev. B **34**, 5947 (1986).

[16] At this low coverage there is no sign of a preference for the adatoms to cluster on the terraces or bind to step edges. This places an upper limit on any adatom transient mobility across the surface during the adsorption process. See W. F. Egelhoff, Jr. and I. Jacob, Phys. Rev. Lett. **62**, 921 (1989), and P. S. Weiss and D. M. Eigler, *ibid.* **69**, 2240 (1992).

[17] Voltage ramps typically required ~10 sec. Drift of the STM tip with respect to the sample was negligible during this time.

[18] R. M. Tromp, E. J. v. Loenen, J. E. Demuth, and N. D. Lang, Phys. Rev. B **37**, 9042 (1988).

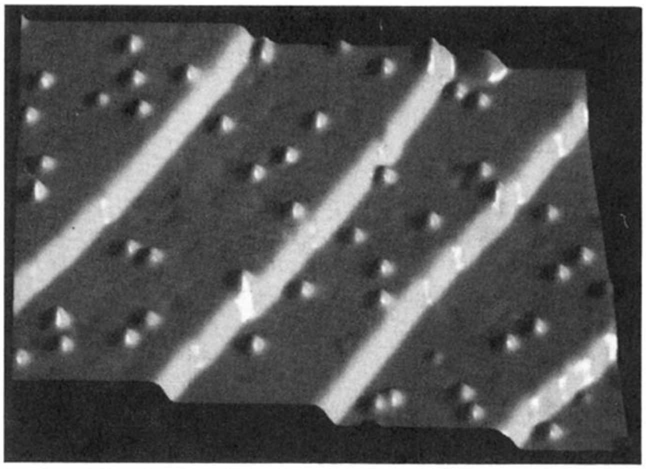
[19] J. P. Pelz, Phys. Rev. B **43**, 6746 (1991).

[20] Single atoms from the tip were deposited onto the surface by gently "contacting" the STM tip to the surface (junction impedance ~ 60 kΩ), and then retracting the tip. This process was tip dependent.

[21] Some justification for assuming a constant $\rho_{\mathrm{Pt}}(E)$ is that the tip was sufficiently far from the surface (~ 6 Å) that one can expect the measured current to be dominated by electrons tunneling to and from s- and p-like states at the surface. For the energy range probed in this experiment ($E_F \pm 1.0$ eV), the bulk densities of these states in Pt are relatively featureless. See A. Brodde, S. Tosch, and H. Neddermeyer, J. Microsc. **152**, 441 (1988); Y. Kuk and P. J. Silverman, J. Vac. Sci. Technol. A **8**, 289 (1990); D. A. Papaconstantopoulos, *Handbook of the Band Structure of Elemental Solids* (Plenum, New York, 1986).

[22] N. D. Lang, Phys. Rev. Lett. **58**, 45 (1987).

[23] B. T. Jonker, K.-H. Walker, E. Kisker, G. A. Prinz, and C. Carbone, Phys. Rev. Lett. **57**, 142 (1986).



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